STUDIES OF ZERO-GRAVITY EFFECTS ON SOLIDIFICATION

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ABSTRACT

The major activities recently initiated within the Space Sciences Laboratory in support of the Manufacturing in Space effort at the Marshall Space Flight Center will be discussed. These efforts are primarily aimed toward scientifically defining the role of gravity in the various processes involving solidification. A motion picture of the solid/liquid interface of several transparent freezing materials will be shown.

INTRODUCTION

The Manufacturing in Space Program presently being formulated within NASA is a concept having tremendous potential. It covers a broad spectrum of ideas and tasks to manufacture products in the unique environment of space where several definite advantages are inherently present. Many disciplines are required to formulate, evaluate, design, and develop a sound and complete program. The disciplines vary from commercial hardware to material science to space science to spacecraft engineering. These must be integrated suitably to produce the very best program possible. This program should 1) define the products to be manufactured in space on a continuous basis, 2) define, analyze, and develop zero-g technology and its associated problems, 3) define the research and development that is required in space, and 4) plan, develop, test, and fly manufacturing-in-space modules and payloads. A strong scientific research program is required and will be a vital part of NASA's overall Manufacturing in Space Program.

The unique space environment of zero gravity, vacuum with infinite pumping speed, solar radiation, solar wind, and low vibration are of most interest. Of these, zero gravity is the most unique and important boundary condition of space. The effects of these special environments on such solidification properties as nucleation and supercooling, freezing stability criteria, contamination, diffusion, etc., poses a fundamental problem in evaluating potential space manufacturing processes. Most of the subject effects are presently in the speculative stage. This research program will initiate analytical and experimental definition of these effects. The experimentation should initially be earthbound and later culminate in space flight experimentation. The following is quoted from the Proceedings of the 1968 Winter Study on Uses of Manned Space Flight:

> "The initial emphasis should be upon research to understand how materials behave during zero-g processing and to identify new materials and fabrication methods to be used later. It does not appear that early emphasis should be placed upon actual fabrication of specific products."

This approach is particularly important because it means that a logical, planned, and coherent research program must be initiated toward the understanding of space environmental effects on the basic mechanisms (rather than researching every aspect of only one product which could possibly not be attractive to the industrial and scientific community in a few years). Nevertheless, a candidate list of highly potential processes and materials to be formed in space is still an essential guideline in studying the effects of the space environment upon basic properties.

There are many candidate tasks and associated problems in the Manufacturing in Space Program that can be properly evaluated only by scientific research and development. This is especially true in the area of crystal growth, perhaps the most important single area of the Manufacturing in Space Program.

More nearly perfect crystals are possible. Artificially grown single crystals are being produced in large quantities to satisfy the needs of solid-state electronics, optics, and structural engineering research (by utilizing the full bonding forces between adjacent atoms in nearly perfect single crystals). Crystal growth is accomplished in a variety of ways for the production of piezoelectrics, semiconductors, laser crystals, whisker crystals, etc.

ZERO-GRAVITY CRYSTAL GROWTH

To ascertain the effects of the space environment upon solidification processes and crystal growth and to determine how these unique boundary conditions can be used to improve the size and perfection of crystals, it is useful to begin by considering the whole field of crystal growth as presented by M. Schieber at the 1966 International Congress of Crystal Growth:

"I. THEORY OF NUCLEATION AND GROWTH

- A. Interface versus Diffusion Process
- B. Mathematical Growth of Crystals
- C. Kinetics of Growth
- D. Morphological Stability Criteria
- E. Three-Dimensional Nucleation
- F. Perturbation of Impurity Flow

"II. EXPERIMENTAL CRYSTAL GROWTH

- A. Melt Growth of Semiconductors
- B. High-Pressure Growth
- C. Vapor Growth
- D. Strain Anneal Growth of Metals
- E. Flux Growth of Ferrites
- F. Zone Melting of Organic Crystals
- G. Automatic Plasma Torch-Verneuil

"III. CHARACTERIZATION OF CRYSTALS

- A. Electrical
- B. Solid-State Physics

C. Perfection of Crystals

D. Properties of Crystals

E. Segregation Coefficients

F. Stoichiometry Magnetism Purity

G. Crystallography of Structure"

Obviously, all three areas are of interest in the Manufacturing in Space Program. In Area I, one expects to find the functional dependence of the subject processes on the imposed boundary conditions, i.e., gravitational perturbation of impurity flow, etc. In Area II, the techniques to be employed in space must be analyzed for adoption to space flight conditions and constraints. In Area III are the techniques by which the crystals are evaluated and characterized.

It is often stated that crystal growth is an art. To some extent this is true. The work in Area I has lagged behind the tremendous advances which have been made in Areas II and III. On the other hand, the volume of knowledge in Area I is fairly extensive and is growing rapidly. The technical status in the field of crystal growth strongly influences the approach which must be taken in developing crystal growth technology for manufacturing in space. A strong ground-based program is required that has initial thrust in Area I, supplemented with carefully planned ground-based experiments in Area II. (The experimental data are evaluated using the approaches listed in Area III.)

The ground-based program approach must recognize that each of the fields listed by Schieber are in themselves broad fields of scientific study. Thus, the program defined here represents a multidisciplinary approach which includes in-house, contractual, and academic personnel. The definition of objectives stated herein utilizes academic consultations. A strong in-house effort is particularly desirable for the following reasons:

1. Research flexibility

2. Contact and communication with the scientific community

3. Task evaluation independent of commercial interests

4. Scientific monitoring of out-of-house contracts

5. Direct assistance to project engineering in the Manufacturing in Space on such missions as the Saturn Orbital Workshop

6. Immediate access to existing information on the space environment

7. Definition of critical problem areas

8. Long-range research continuity

With these factors in mind, Space Sciences Laboratory (SSL) has initiated a ground-based research program whose objectives are to answer, insofar as technically possible, the following basic questions by analytical and experimental study and by personal contact with various experts within the scientific community:

1. What are the effects of gravity on solidification and crystal growth?

2. How can these effects be utilized to improve the size, quality, and purity of industrial-type crystals?

3. What are the observable dependent parameters affected by gravity?

4. What are the synergistic effects of gravity with other boundary condition changes?

5. What theoretical and analytical predictions are possible on gravitational effects?

6. What supporting ground-based experimentation is required?

7. What flight data are required?

In the ensuing pages, studies initiated to answer these questions in the areas of solidification, single crystal growth (bulk crystals), and single crystal growth (whisker crystals) are discussed.

ANALYTICAL STUDIES

A continuing effort is being made to keep abreast of the literature and to perform pertinent analysis. At present, considerable effort is spent on this aspect of the program by SSL personnel and in contractual studies being performed by Dr. Grodska of Lockheed. The inhouse studies are

concentrating on defining the influence of thermal convection and fluctuations upon parameters such as diffusion which affect the deposition of impurities and dopants in crystal growth.

For example, Burton, Prim, and Slichter have shown that a relation can be established between the interfacial distribution coefficient k and properties of the liquid melt:

$$k_{eff} = \frac{k}{k + (1-k)\, e^{-\frac{f\delta}{D\,\frac{\rho_s}{\rho_L}}}}$$

where

$k = C_s/C_L$

C_s = impurity concentration in the solid

C_L = impurity concentration in the liquid

δ = effective thickness of the diffusion layer

f = growth rate

ρ = density

D = effective diffusion coefficient of the impurity.

The term k_{eff} determines the rate at which impurities (or dopants) are deposited during solidification. Both δ and D are usually very susceptible to the smallest fluctuations [1] in the liquid melt, meaning they are influenced by gravity-induced convection. It is noted that several expressions exist in the literature [2] for k_{eff}, depending on particular material properties such as anisotropic growth rate. The above expression is given as an example of this type of relationship.

It may be asked why solidification in zero-g cannot be simulated on earth by maintaining the lower densities upward where gravity-induced convection is eliminated. The answer is that laminar flow, as described by Rayleigh, for all intents and purposes, is eliminated. However, the types of flow that hinder crystal growth are thought to be fluctuations, turbulences, and eddy currents that are present because of various driving forces such as thermal gradients, surface tension, and capillarity, all of which give rise to flow such as Marangoni flow and Benard cells. These fluctuations do not occur homogeneously and are perturbated by gravity. Thus, crystal growth in zero-g is unique.

The Lockheed effort is aimed toward the broader goal of defining space environmental effects on solidification, emphasizing the role of gravity upon interface shape, dislocation formation, component segregation, growth rate, nucleation, etc., and to predict the effect of these factors on the solidification of semiconductors, superconductors, ferroelectrics and other candidate space processing materials. This effort requires a short precursory study to assemble a list of the present candidate materials to which this knowledge must be applied. The principal investigator is Dr. P. Grodska, who is speaking at this meeting.

ZERO-G DROP TOWER

This project is a joint experimental effort of the Space Sciences and Manufacturing Engineering Laboratories to generate data on the solidification in zero-g (in vacuo) of small drops of high melting point metals. The research objectives are divided into the following:

1. Geometry and shape of drops. The degree of roundness which a freely falling drop will attain due to cohesion, surface tension, and viscosity upon freezing is to be analyzed. Most models used for defining this roundness are functionally dependent upon the initial distortion and the average radius of the sphere. Thus, the results obtained from the spheres formed in the drop tower should provide useful data applicable to the larger spheres to be formed in space on AAP-2. Of particular concern here is the comparison of the time for this initial distortion to dampen with the time to nucleation. A variety of shapes will be obtained if the initial distortions are not dampened.

2. Grain structure. Among the factors influencing grain structure are a) quenching after freezing, b) rate of freezing, c) nucleation, and d) heat transfer within the sphere during freezing (reference is made to personal conversations with M. C. Fleming of MIT). We intend to make comparative

analyses on drops frozen in 1-g and 0-g in which (a) and (b) are made the same. We hope that nucleation effects will be sufficiently repeatable to make deductions concerning (d). As a later project, a second-generation catching device will be designed to prevent rapid quenching after the sphere is frozen.

3. Hollow areas. It is not unlikely that thermal contraction effects, together with small thermal asymmetry effects, can cause the appearance of hollow regions during freezing in free fall. Some thermal asymmetry can be expected because the initial nucleation sites are random, and, as growth progresses from these sites, the latent heat is liberated asymmetrically with respect to the center of the sphere.

4. To observe possible supercooling effects by varying the time of fall.

The SSL/ME drop tower is located in Building 4331 (Figure 1). The tower is designed to obtain the desired spheres without the use of a falling canister; only the sphere falls. This approach eliminates the problem of positioning the sphere relative to a canister. To elimate air drag, gaseous convection, and oxidation, a vacuum of at least 10^{-5} torr is required in the drop tube. The drop distance ℓ was established at 4.9 m (16 ft) [extension to 6.1 m (20 ft) may be accomplished later] where 1-sec drop time t is attained; that is,

$$t = \sqrt{2\ell/g}$$

Sphere diameters of the order of millimeters are possible as illustrated in the following calculation:

For a metallic sphere having the following geometrical and material properties,

r = radium (m)

ρ = density (kg/m^3)

Q_F = heat of fusion (kcal/kg = cal/g)

ϵ = emissivity

T = temperature of freezing (°K)

M mass (kg)

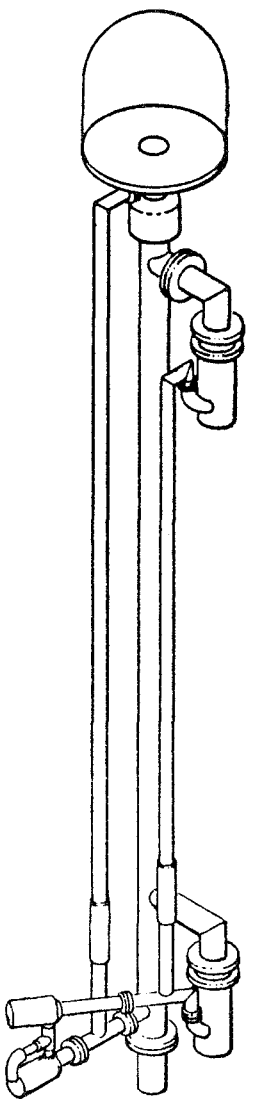

FIGURE 1. Joint SSL/ME zero-g drop tower for space processing ground-based studies

other parameters:

Q = heat energy (joules)

t = time (sec)

A = surface area (m^2)

σ = Stefan-Boltzmann constant ($W/m^2 \circ K$)

T' = temperature of the tube.

The amount of heat energy to be radiated away from the sphere to accomplish total freezing is

$$Q = (4.18 \times 10^3)\, Q_F M$$

$$\cong 5\pi Q_F \rho r^3\, 10^3 \qquad (1)$$

This quantity is also equal to the time integral of the dissipation rate by the Stefan-Boltzmann relation for a freely falling sphere in vacuo

$$\frac{dQ}{dt} = A \epsilon \sigma (T^4 - T'^4) \quad ,$$

Now

$$T^4 >> T'^4$$

$$\therefore \frac{dQ}{dt} \cong A \epsilon \sigma (T)^4$$

or

$$\frac{dQ}{dt} = \pi r^2 \epsilon \sigma T^4$$

Upon integrating from t=0 to t=t,

$$Q = \pi r^2 \epsilon \sigma T^4 t \quad . \tag{2}$$

Combining equations (1) and (2),

$$r = \frac{\epsilon \sigma T^4 t}{5 Q_F \rho 10^3} \quad .$$

Finally, for a sphere having

$Q_f = 10$ kcal/kg (=10 cal/g)

$\epsilon = 0.1$

$T_f = 2000\ ^\circ K$

$\rho = 7 \times 10^3$ kg/m^3

$$r = \frac{(10^{-1})\ (5.67\ 10^{-8})\ (2)^4\ (10^{12})\ 1}{5\ (10)\ (7)\ (10^3)\ (10^3)}$$

$= 3 \times 10^{-4}$ m $= 0.3$ mm

or $d = 0.6$ mm.

It is anticipated that $\epsilon = 0.1$ is a worst case and $\epsilon = 0.4$ is probably more reasonable for the materials, in which case, $d = 2.4$ mm.

EXPERIMENTAL CRYSTAL GROWTH

The experimental growth presently encompasses three tasks. Each of these tasks has been defined to obtain data on a specific aspect of zero-g crystal growth, and the approach that is used is to perturbate a boundary condition causing a change similar to that caused by zero-gravity environment. Each of these tasks is supported analytically and is designed as the first-step, ground-based experimentation toward defining the designated objective.

The first task is a contractual study entitled "Effect of Zero Gravity on Single Crystal Whisker Growth," being conducted at the University of Alabama; the principal Investigator is Dr. J. Davis, who is also speaking at this meeting. Single-crystal whiskers have tremendous industrial potential because of their high degree of crystalline perfection which gives them tensile strength two orders of magnitude higher than the bulk crystal.

The second task in the area of crystal growth experiments is entitled "Bulk Crystal Growth in Zero-g." The Principal Investigator is Dr. U. Roy of the University of Alabama at Huntsville. Dr. Roy's group is working very closely with SSL in-house efforts. Primarily, he is attacking the question of zero-g effects on the growth of large single crystals by defining and performing specially selected experiments in the laboratory that will elucidate the role of gravity. Dr. Roy will discuss this in greater detail in another presentation at this meeting.

The third task is an in-house effort defined to experimentally determine the effects of the magnitude thermal convection on impurity deposition in semiconductors. This task was defined in SSL and will be performed in Marshall's Astronautics Laboratory where the required equipment is available. By holding all boundary conditions constant except the thermal gradient in the crucible, it is anticipated that single crystals can be grown and characterized according to growth condition. We plan to use the Czochralski growth method, as it is one of the better techniques for growing high-quality semiconductors. However, this technique, in its present form, is not attractive for space flight because of the amount of machinery required. It is very possible that a modified approach will materialize that will be compatible with space flight. The material chosen for this study is In Sb which exhibits impurity banding, has a melting point of 525° C, and no vapor pressure problems. [3] Compared with Ga As, In Sb experiments should yield vital information, be easier to grow, and should provide a basis for in-house capability necessary for this type of project.

FLIGHT EXPERIMENT

A flight experiment presently under development in SSL is T-038, "Zero Gravity Crystal Growth." This experiment is designed to study the solidification of materials in orbit whose behavior is highly observable and whose handling is relatively simple. The experiment is also designed to visually and photographically observe through a microscope the freezing of transparent materials. Laboratory movies (time lapse) are presently available in which studies are documented on the behavior of such materials as

hexadecane, lithium nitrate trihydrate, and water. Bubble formation, convection, nucleation, autonucleation, and growth rates are easily observed. (Similar studies have been made in a centrifuge where smaller grain sizes were observed.) We propose to perform these experiments in zero-g to obtain data for analysis. The flight configuration is designed to accommodate several materials including a low melting point metal and perhaps a whisker experiment.

Space Sciences Laboratory is also involved in the M512 crystal-growing experiment approved for AAP-2 as alternate investigator and alternate COR. The Solid State physics group of SSL-TR has been considering post-flight analysis of the crystals resulting from this experiment. Dr. Kulshreshtha will expand on this subject later in this meeting.

REFERENCES

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